REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Paper	

4. TITLE AND SUBTITLE

Please see attached

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2308

5e. TASK NUMBER
M19B

5f. WORK UNIT NUMBER
346058

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

ERC

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
Please see attached

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

2308M19B

MEMORANDUM FOR PRS (Contractor/In-House Publication)

FROM: PROI (STINFO) 27 June 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2001-153**
Ghanshyam L. Vaghjiani, "Investigations of Chemiluminescence in the CH_2 + O Gas Phase Reaction"

37th AIAA/ASME/SAE/ASEE JPC & E **(Statement A)**
(Salt Lake City, UT, 08-11 Jul 2001) (Deadline: 30 June 2001)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments:_____

Signature _____ Date _____

2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review.
Comments: _____

Signature _____ Date _____

3. This request has been reviewed by the STINFO for: a.) changes if approved as amended, b) appropriateness of references, if applicable; and c.) format and completion of meeting clearance form if required
Comments:_____

Signature _____ Date _____

4. This request has been reviewed by PR for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/ national critical technology, and f.) data rights and patentability
Comments:_____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

_____

PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

AIAA-2001-3710

Investigations of Chemiluminescence in the $CH_2 + O$ Gas Phase Reaction

Ghanshyam L. Vaghjiani
ERC, Inc.
Air Force Research Laboratory, AFRL/PRSA
10 E Saturn Blvd
Edwards AFB, CA 93524
Tel: (661) 275 5657
Fax: (661) 275 6245
Email: ghanshyam.vaghjiani@edwards.af.mil

37th AIAA/ASME/SAE/ASEE
Joint Propulsion Conference & Exhibit
July 8-11, 2001 / Salt Lake City, UT

AIAA-2001-3710

INVESTIGATIONS OF CHEMILUMINESCENCE IN THE CH_2 + O GAS PHASE REACTION

Ghanshyam L. Vaghjiani
ERC, Inc., Air Force Research Laboratory, AFRL/PRSA, 10 E Saturn Blvd, Edwards AFB, CA 93524
Tel: (661) 275 5657, Fax: (661) 275 6245, Email: ghanshyam.vaghjiani@edwards.af.mil

ABSTRACT

The reaction of ketene (C_2H_2O) in a known excess of O-atoms was studied in a discharge flow-tube apparatus. Characteristic CO-chemiluminescence was observed in the range 130-900 nm. The rate coefficient for this reaction was determined to be (6.82 ± 1.02) x 10^{-13} cm^3 $molec^{-1}$ s^{-1} at 295 K by recording the relative strength of the steady-state 216-nm Cameron emission as a function of the reaction length in the flow-tube. The band structure of the emission spectrum recorded suggests that the subsequent very rapid reaction of O-atoms with the product, C_2O and possibly with CH_2, that are formed in the initial C_2H_2O + O oxidation lead to the observed radiation. 351-nm pulsed laser photolysis of the unreacted ketene in the detection volume of the apparatus resulted in transient enhancements of the CO-chemiluminescence. The time behavior of these emissions and their dependence on the laser fluence employed was consistent with the photolytic production of CH_2 and also C_2O, respectively, due to 1-photon and 2-photon absorption of the 351-nm laser radiation by the ketene. Strong OH(A) emission was also seen in these experiments when excess O_2 was present. The reaction of CH with O_2 is responsible for this emission. The principal source for CH in our system is thought to be the CH_2 + O reaction.

INTRODUCTION

The interactions of carbonaceous combustion species in rocket plumes with the atmosphere are thought to play an important role in the production of ultraviolet, visible, and infrared radiation signatures at high altitudes. A detailed understanding of the pertinent chemical reactions that produce the electronically excited species, and of the competing quenching reactions that remove the internal energy in radiation-less processes is needed to accurately calculate short wavelength plume spectral signatures and absolute radiances and their temporal/spatial evolution in the high atmosphere. To facilitate these efforts, we are currently carrying out laboratory investigations to elucidate the reaction mechanisms in the oxidation of CH, CH_2, C_2H, and C_2O with O-atoms and O_2. Sufficient exothermicity in CH, CH_2, and C_2H reactions (except C_2H + O) is available to produce CO in one or more of the triplet states (a, a', and d). Even more reaction enthalpy is available in C_2O reaction(s) to produce higher excited states of CO (e, A, I, and D). Other excited species such as $CH(A^2\Delta)$ in C_2H + O (or + O_2), and $OH(A^2\Sigma^+)$ in CH + O_2 reactions are also possible. uv-CO-chemiluminescence has previously been identified in the C_2H + O_2 reaction,[1] and both uv- and vuv-CO-chemiluminescence in the C_2O + O reaction.[2-7] However, only limited information is available on the product branching ratios of the excited CO states responsible for the emission.[7] Estimates of the branching ratio of $CH(A^2\Delta)$ formation in the reactions of C_2H with O and O_2 can be found in the literature.[8-10] To our knowledge, triplet CO formation in CH and CH_2 reactions has not yet been positively identified. Fast discharge-flow tube and pulsed-laser photolysis methods have been employed in this work to study the reaction kinetics and chemiluminescence in these and C_2O reactions.

EXPERIMENTAL TECHNIQUE

The discharge flow-tube apparatus employed in this work has previously been described in detail elsewhere.[11] A schematic of the apparatus is shown in Figure 1. Here, we only provide details of the experimental procedures employed to record the chemiluminescence data. A small flow of C_2H_2O in helium was carried into an absorption cell for 213.9-nm photometric determination of its gas phase concentration before sending it for further dilution via a sliding injector into the main reaction section of a flow-tube that carried a known excess flow of He. A value of $\sigma_{213.9\ nm} = 889.2 \times 10^{-20}$ cm^2 $molec^{-1}$ was used for the C_2H_2O uv-absorption cross-section.[12] A fixed side-arm microwave discharge port was used to introduce an excess of $O(^3P)$ into the flow-tube. $O(^3P)$ was made from the discharge of a 1% mixture of either O_2 or N_2O in He. The $[O^3P]$ in the flow-tube was determined by NO_2 titration; $O + NO_2 \rightarrow NO + O_2$. The end-point of this reaction was followed either by monitoring the yellowish-green emission in the accompanying, $O + NO \rightarrow NO_2 + h\nu$ reaction, or by direct vuv cw-resonance fluorescence detection of the $O(^3P)$. The electronic mass flow meters, capacitance manometers and the chromel-alumel thermocouples used to flow the gases, and measure the flow-tube system's pressure and temperature had previously been calibrated. A typical linear velocity, $v = 800$ cm s^{-1} for the bulk flow rate of the He gas was maintained through the 1-inch-diameter flow-tube at a nominal pressure of 2.0 Torr to ensure that the flow-tube was being operated under plug-flow conditions at the ambient temperature of 295 K.[13] For the data reported here, the $[O^3P]/[C_2H_2O]$ ratio ranged from 20 to 200, where the $[O^3P]$ was between (3.5-23.5) x 10^{13} molec cm^{-3}.

The steady-state chemiluminescence produced when C_2H_2O interacted with the O-atoms at a fixed reaction length, z, in the flow-tube was observed downstream at the detection zone using 2 suitable scanning monochromator/PMT detector assemblies that covered the entire 130-900 nm range of interest. Signals from the PMTs were analyzed using photon-counting/multi-channel averaging techniques.[14] The instrument resolutions were ~ 1.9 and ~ 1.1 nm, FWHM, respectively, in the uv and the visible portions of the spectrum. Suitable cutoff filters were placed at the entrance slit of the monochromator to avoid detection of the uv radiation through second order transmission when recording in the visible region. Figures 2, 3, 4, and 5 show the typical emissions observed. The kinetics of this reaction was followed by recording the relative strength of the 216-nm emission as a function of the reaction length in the flow-tube for a series of chosen O-atom concentrations. Figure 6 shows the exponential dependence of the emission intensity with the reaction time, $t = z/v$.

A 351-nm pulsed laser beam (20-50 mJ/pulse and operating at 10 Hz) was focused at the detection zone to photolyze any unreacted ketene to look for transient enhancements in the CO-chemiluminescence at a selected few emission band centers. A 10-μsec dwell-time was employed in the multi-channel averager to properly resolve the time profile of the transient emissions. The time behavior of the transient signal was recorded by co-adding typically 50000 pulses to improve the signal-to-noise ratio of the data. Figures 10, 11, and 12 show the transients recorded at 788, 216, and 165 nm.

Materials

He (>99.9997%) carrier gas from U. S. Bureau of Mines was used as received. NO_2 (99.9%) from M. G. Scientific Gas was mixed with excess O_2 to react away any NO present and the mixture collected in a trap over silica gel at 213 K. The excess O_2 and any other volatiles were pumped off and the condensate subjected to several freeze-thaw purification cycles at a greaseless vacuum line. A standard 10% NO_2 in He titration mixture was prepared. O_2 (99.991%) from Big Three Industries and N_2O (99.99%) from Matheson Gas Products were used as supplied to make up 1% in He discharge mixtures. Ketene was prepared by pyrolytic decomposition of acetone (HPLC grade) over a heated (970-1020 K) Chromel-A wire in a reflux apparatus. The effluents from the apparatus were first passed through a trap maintained at 270 K to remove most of the unreacted acetone, and then through another trap maintained at 173 K to collect the ketene. The condensate was subjected to several freeze-thaw purification cycles to remove the remaining acetone and any CO_2 collected during the synthesis. The uv spectrum of the purified sample was measured in the range 140-400 nm.[12] No characteristic acetone absorption features were seen. The sample purity of the ketene was estimated to be ~ 99% from the calculated absorption cross-sections. A 10% ketene in He reaction mixture was prepared.

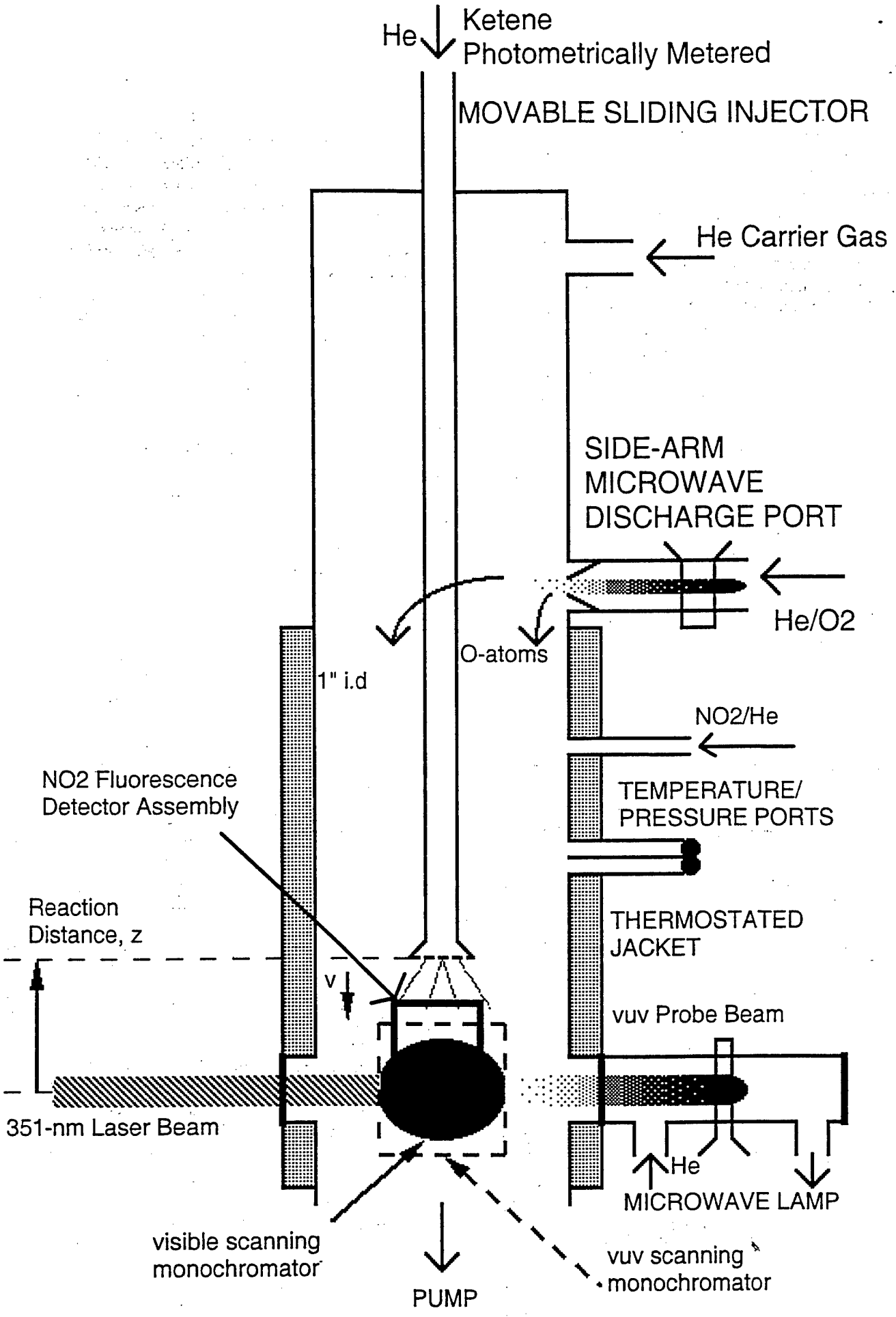

FIG. 1. Discharge flow-tube/pulsed photolysis apparatus.

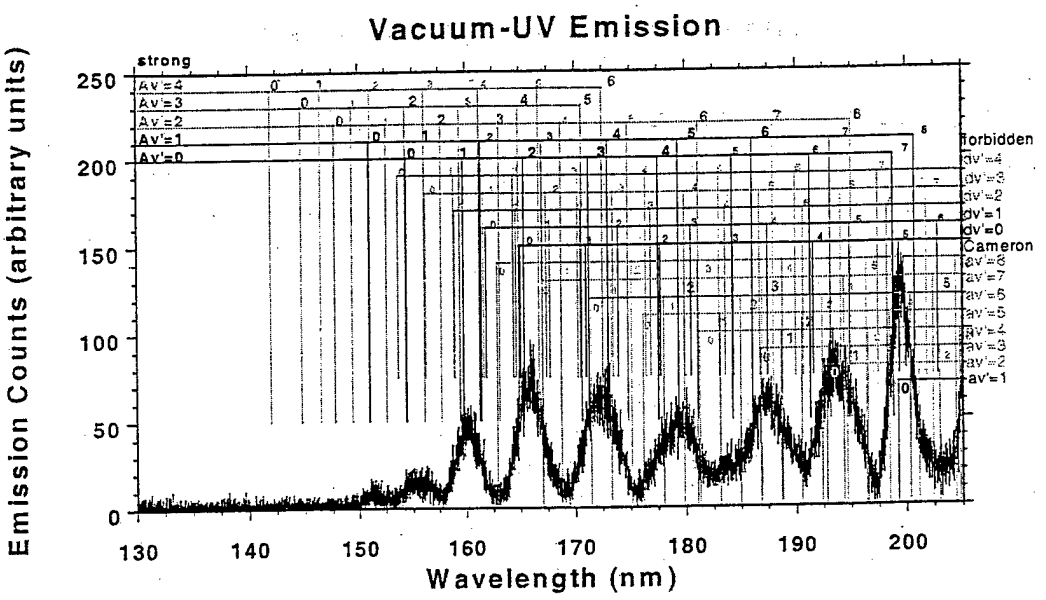

FIG. 2. vuv-CO-chemiluminescence observed during C_2H_2O + O-atom reaction.

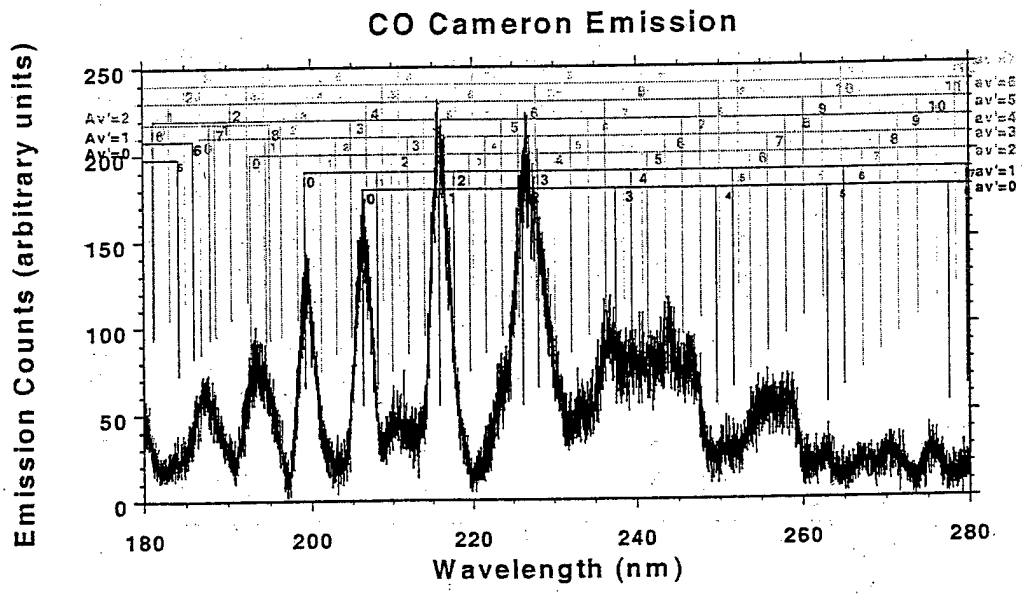

FIG. 3. uv-CO-chemiluminescence observed during C_2H_2O + O-atom reaction.

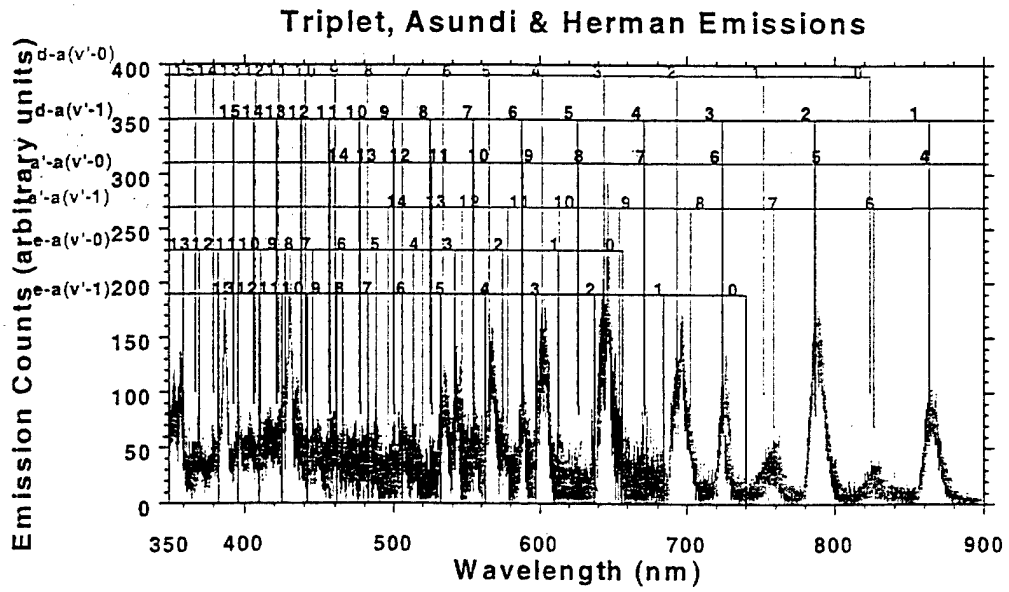

FIG. 4. Visible-CO-chemiluminescence observed during C_2H_2O + O-atom reaction.

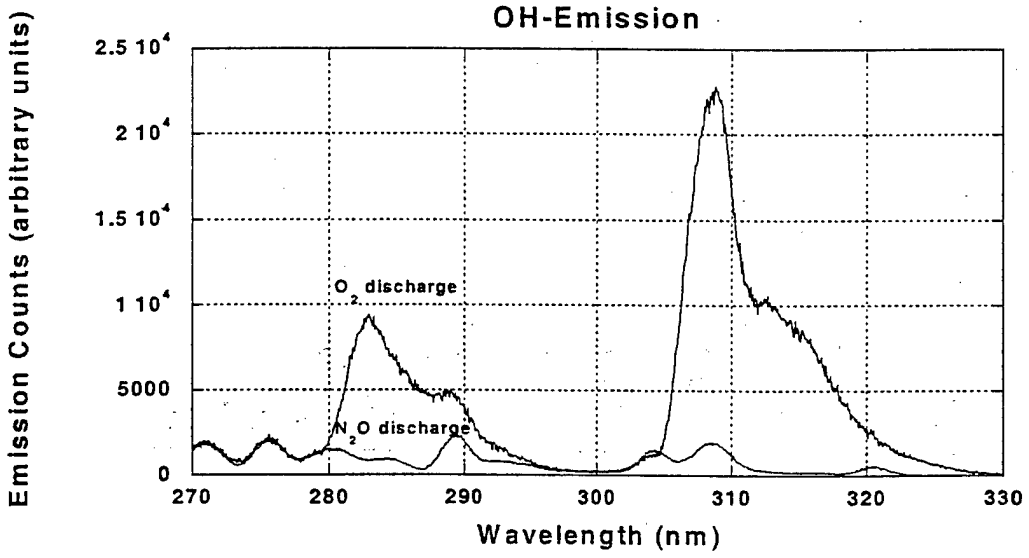

FIG. 5. uv-OH-chemiluminescence observed during C_2H_2O + O-atom reaction.

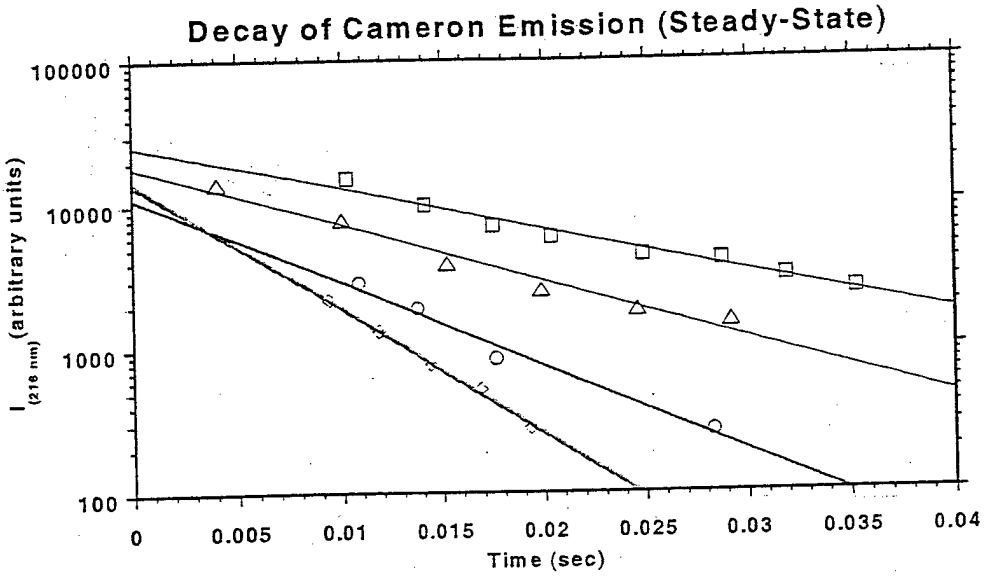

Fig. 6. Decay of 216-nm-CO-emission as a function of flow-tube reaction time for four different O-atom concentrations.

RESULTS AND DISCUSSION

Flow-tube work

Even though CO may form directly in the C_2H_2O + O-atom interaction, the reaction exothermicity is insufficient to produce the electronically excited product. Thus, the source of emission in Figures 2, 3, and 4 must be from the subsequent reaction of excess O-atoms with the product(s) in this reaction. If the oxidation rate of ketene by O-atoms is much slower (and therefore rate limiting) compared to that of the product(s), it can be shown that the steady-state emission strength in the flow-tube for long reaction times will follow an exponential relationship with a decay coefficient given by $k' = k + k_1[\text{O-atom}]$. k' is the pseudo-first-order loss rate term for C_2H_2O in the flow-tube, where k is the loss rate term in the absence of O-atoms, and k_1 the absolute second-order rate coefficient for C_2H_2O + O-atom reaction. Figure 6 shows how the 216-nm emission, due to the CO(a, v' = 0 → X, v" = 1) transition, varied as a function of the reaction time in the flow-tube for different O-atom concentration conditions. The straight lines are exponential fits to the data points where the slopes yield values for the first-order loss rate terms for C_2H_2O. In Figure 7 these values are plotted as a function of the [O-atom] employed to extract the second-order rate coefficient from the fit of the data points to a straight line. A value of k_1 equal to (6.82 ± 1.02) x 10^{-13} cm^3 $molec^{-1}$ s^{-1} at 295 K was determined. This value is in excellent agreement with previous determinations by Carr and co-workers (8.8 x 10^{-13}),[15] Mack and Thrush (5.7 x 10^{-13}),[16] and Washida and co-workers (4.3 x 10^{-13} cm^3 $molec^{-1}$ s^{-1}).[17]

The possible products in the ketene plus O-atom reaction are shown below:

$$C_2H_2O + O \rightarrow CH_2 + CO_2 \quad \Delta H = -49.2 \text{ (kcal mol}^{-1}\text{)}$$
$$\rightarrow CH_2O + CO \quad -100.6$$
$$\rightarrow H_2O + C_2O \quad -14.0$$
$$\rightarrow HCO + HCO \quad -28.2$$
$$\rightarrow HCO + H + CO \quad -10.7$$

Mack and Thrush[16] did not observe any significant amount of water formation in their work.

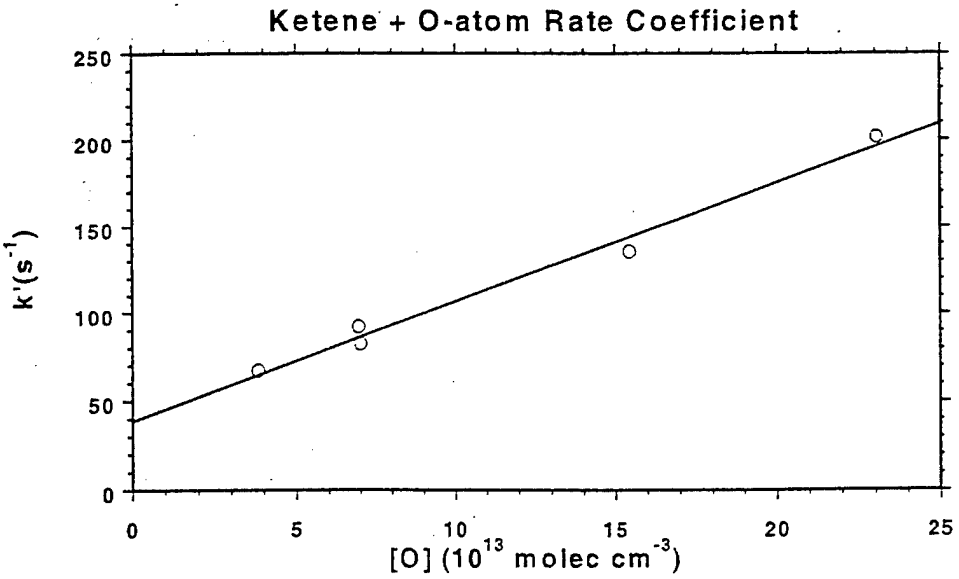

FIG. 7. A plot of k' versus [O] employed in Figure 6.

Therefore the formation of C_2O (the co-product in the third channel) is expected to be negligible in this reaction. Carr and co-workers[15] and Washida and co-workers[17] have directly determined the formaldehyde yield to be ~ 20% and ~ 15%, respectively. The latter group also directly determined the total HCO yield to be ~ 10%. Thus the second, fourth, and fifth channels are also minor processes in ketene oxidation by O-atoms. Furthermore, the product studies of Mack and Thrush also showed a high yield for CO_2.[16] However, they rationalized this to be due to the subsequent oxidation of the formyl radical, which they assumed to be the dominant initial product in their experiments:

$$HCO + O \rightarrow H + CO_2 \quad \text{(branching fraction ~ 50\%)}$$
$$\rightarrow OH + CO \quad (\sim 50\%)$$

The HCO can also arise from subsequent formaldehyde oxidation:

$$CH_2O + O \rightarrow OH + HCO \quad \text{(branching fraction >95\%)}$$
$$\rightarrow H + HCO_2 \text{ (or } H + CO_2) \quad (<5\%)$$

One can reconcile the differences of these two studies by proposing the first channel to be the dominant source of CO_2. This would imply that CH_2 is a major product in the ketene + O-atom reaction. The reaction of CH_2 + O is known to be very fast[18] and exothermic enough (by ~ 179.3 kcal mol^{-1}) to possibly excite the known CO product into its triplet states. We should then expect to see Cameron emissions from CO(a, $v' \leq 8$), Asundi emissions from CO(a', $v' \leq 6$), and Triplet emissions from CO(d, $v' \leq 1$) in the room temperature ketene plus O-atom reaction. The data of Figures 4 and 2, however, show emissions arising from even higher levels. There are two possibilities for this in our apparatus. One is that the C_2H_2O + O reaction produces internally excited CH_2. The 49.2 kcal mol^{-1} of energy available could allow vibrationally excited $CH_2(^3B)^{\ddagger}$ to be formed with up to ~ 9.0 kcal mol^{-1} of internal energy. Excitation in excess of this would promote the methylene (directly or in energy transfer collisions) into the first excited singlet (^1A)-state, which would rapidly quench back to the (^3B)-state under our flow-tube conditions.

If excited $CH_2(^3B)^{\ddagger}$ reacts with the O-atoms, CO(A, $v' = 0$) formation would be possible.

This would predict the shortest, 4th-Positive, CO-emission wavelength of ~ 151.8 nm in the vacuum-uv. Of course, correspondingly higher v' excitations in (a), (a') and (d) triplet states would also occur compared to that in the ground-state reaction of $CH_2(^3B)$. However in Figure 2, we still see emission to the blue of this threshold, which implies that yet another species' reaction with O-atoms is important in our system. The most likely candidate for this is the C_2O + O-atom $\rightarrow$ CO + CO* reaction, which would have an emission threshold at ~ 139.7 nm. In Figure 8 the data of Figure 2 is re-plotted on a logarithmic scale in the region 130-165 nm. The non-zero signal for wavelengths shorter than 139.7 nm possibly indicates the involvement of internally excited C_2O. The data below ~ 146 nm is unresolvable with the present spectrometer resolution which was chosen so as to have sufficient throughput for enough detection sensitivity (i.e. S/N = 1, for 1-second integration) and at the same time be able to resolve the broader and stronger bands in the long wavelength region.

We are currently investigating[19] the direct LIF-detection of C_2O formation in our C_2H_2O + O-atom flow-tube setup to confirm the above explanation for the source of high-energy vuv-emissions we have observed. In the next section we describe the results of a pulsed photolysis approach we have used to form transient amounts of CH_2 from ketene photodissociation at 351 nm[20] to see if CO-chemiluminescence can be uniquely assigned to the CH_2 + O-atom reaction.

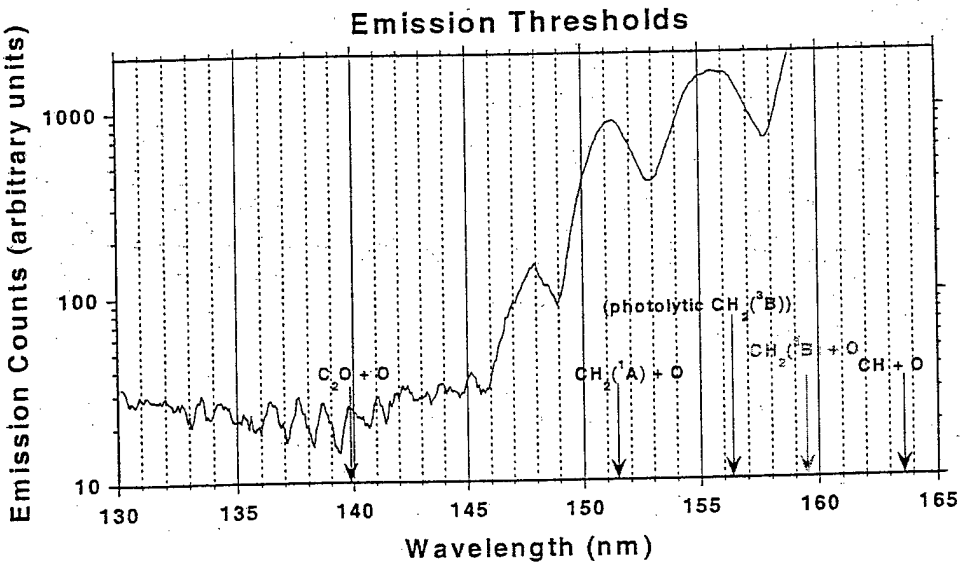

FIG. 8. Comparison of the vuv-emission spectrum obtained in this work to expected emission thresholds for various possible reactions of carbonaceous species with O-atoms in our flow-tube.

In addition to the CO-chemiluminescence, characteristic OH(A) emissions in the (1→0), (0→0), and (1→1) bands were also seen when O_2 was present, i.e. when an O_2-discharge source was used to produce the O-atoms. It is known that in this source, typically 80-90% of the O_2 remains undissociated. When a N_2O-discharge source was used to produce the O-atoms no OH emission was

seen (see lower trace in Figure 5, which shows only the underlying CO-emissions in this region). However, in this case, when a small amount of O_2 was deliberately added to the flow-tube via a side-inlet, strong OH(A) emissions ensued. The following mechanism is proposed for the observed emission. The CH_2 produced in the C_2H_2O + O-atom reaction rapidly reacts with the excess O-atoms to form CH + OH also.[21] The CH can further react with the O_2 to form OH(A).[22] The observed dependence of the OH(A) intensity with the $[O_2]$ used (see Figure 9) was consistent with that expected from a kinetic simulation of the above reaction steps. Note that in the absence of O_2, the main loss mechanism for CH would be via its fast reaction with O-atoms.[23] This reaction, in principle, can also produce CO-chemiluminescence with an emission threshold at ~ 163.8 nm. We plan to look for CO-chemiluminescence in this reaction in the absence of CH_2 (or C_2O) plus O-atom interference(s).[19]

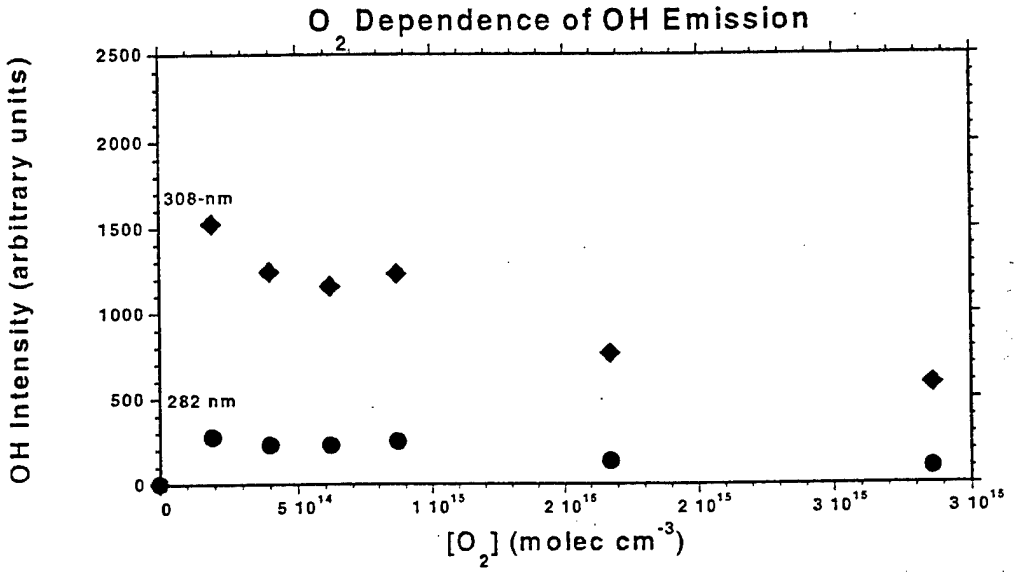

FIG. 9. Dependence of the OH(A) intensity as a function of the O_2 concentration employed in the flow-tube.

Ketene photolysis work

The time behavior of the emission in Figures 10 and 12 is consistent with the direct formation of excited CO in the reaction of the photodissociation product of ketene and O-atoms. The fast rise in the signal corresponds to the short-lived nature of the emitting states. The rate of decay in the signal at long times was exponential and found to be directly proportional to the O-atom density. The slow rise in signal of Figure 11 is consistent with the meta-stable nature of the CO(a) emitting state, which may either form directly in the O-atom reaction or via cascading from the higher (a') and (d) states which are short lived (τ_{rad} ~ 6 μ-sec) and emit in the visible.

It is well established that 351-nm photolysis of ketene produces the ground-state CH_2 radical.[20] If the CH_2 + O-atom reaction is responsible for the emissions of Figures 10, 11, and 12, then a linear dependence of the emission intensity with the laser fluence is to be expected. In Figure 14, the 165-nm signal shows a (laser fluence)$^{1.4}$ dependence,

indicating that there is an additional precursor, X, reaction with the O-atoms involved. This precursor must have its origin in a 2-photon absorption process. We postulate the identity of X to be C_2O. If this is the case then time-resolved emissions to the blue of the 156.6-nm threshold (for photolytic-CH_2 + O-atoms) should be observable. Indeed, emission at 148 nm was seen in the photolysis experiment with a fast rise time (< 10 μ-sec). Its intensity showed a (laser fluence)$^{2.2}$ dependence.

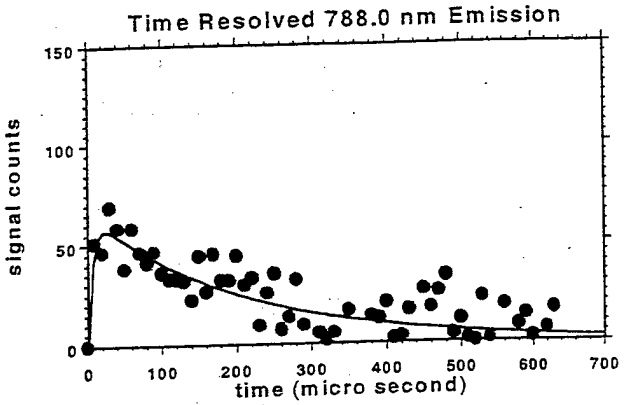

FIG. 10. Transient 788-nm emission during 351-nm C_2H_2O photolysis in excess O-atoms.

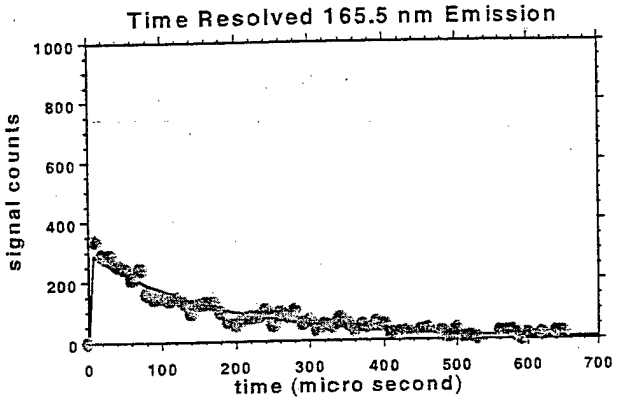

FIG. 12. Transient 165-nm emission during 351-nm C_2H_2O photolysis in excess O-atoms.

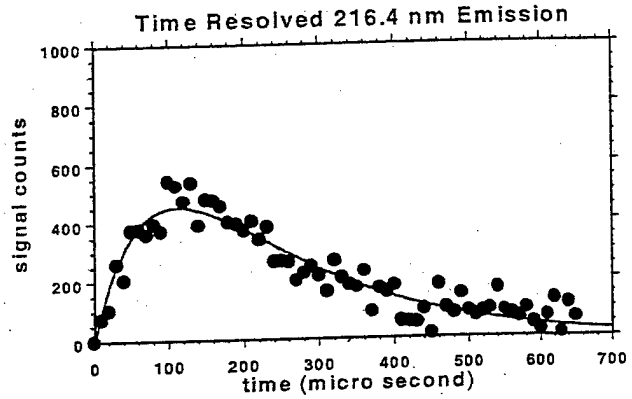

FIG. 11. Transient 216-nm emission during 351-nm C_2H_2O photolysis in excess O-atoms.

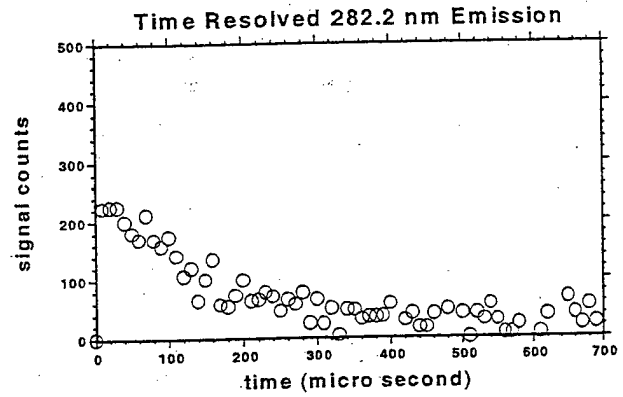

FIG. 13. Transient 282-nm emission during 351-nm C_2H_2O photolysis in excess O-atoms.

Because of the fast rise time, we further postulate that the C_2O is formed directly in the 2-photon dissociation of C_2H_2O. Another source for C_2O could be the HCCO + O-atom reaction, where HCCO forms in the 2-photon dissociation of ketene. However, if this was the principal source for C_2O, then a relatively slow rise in the 148-nm signal would be expected since the rate of the HCCO + O-atom reaction would determine the growth rate of C_2O in the reactor.

The photolysis experiment also allowed us to further verify that the source of OH(A) emission in our experiments is the CH + O_2 reaction. The rise time of the 282-nm-OH signal in Figure 13 was consistently slower than that of the 165-nm-CO signal. Furthermore, the 282-nm-OH signal intensity varied linearly with the photolysis fluence employed (see Figure 15). This is consistent with the notion that the photolytic-CH_2 concentration varies linearly with the 351-nm laser intensity and therefore the CH yield through the CH_2 + O-atom → CH + OH reaction.

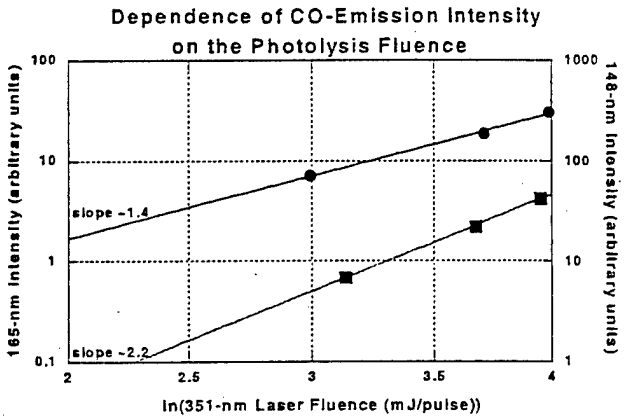

FIG. 14. The dependencies of the 148-nm- and 165-nm-CO emission intensities with the 351-nm laser fluence employed during C_2H_2O photolysis in excess O-atoms. The laser beam was focused at the center of the detection zone to improve the signal level of the CO-chemiluminescence.

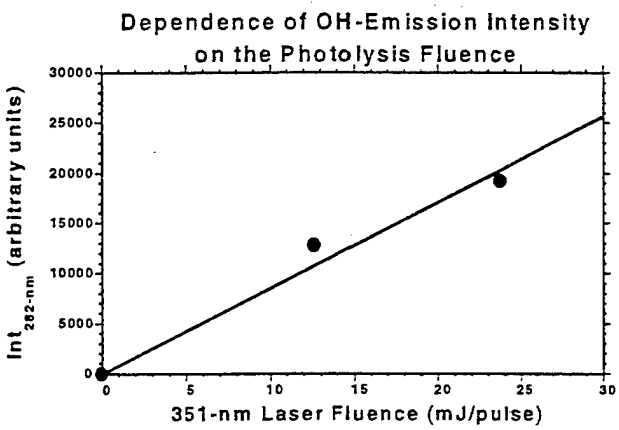

FIG. 15. Linear dependence of the 282-nm-OH emission intensity with the 351-nm laser fluence employed during C_2H_2O photolysis in excess O-atoms. An unfocused laser beam is used in the photolysis.

CONCLUSIONS

The interference from the C_2O + O reaction in our C_2H_2O + O-atom flow-tube setup, and in the high-fluence 351-nm laser photolysis of C_2H_2O in excess O-atoms has prevented us from uniquely assigning the observed CO-chemiluminescence to the CH_2 + O-atom reaction. However, the intermediate, i.e. between linear and quadratic, dependence of the 165-nm-CO emission intensity on the photolysis fluence employed does indicate that the CH_2 + O reaction may have a CO-chemiluminescence reaction channel. We plan[19] to improve the sensitivity of our apparatus for CO-chemiluminescence detection, and then carry out low-fluence 351-nm photolysis of ketene (to suppress any 2-photon processes) and then verify the linear dependence of the CO-emission intensity with the photolysis fluence employed.

This work has also shown for the first time that C_2O can form in the 2-photon 351-nm dissociation of C_2H_2O. We have also shown that C_2O is a possible product in the C_2H_2O + O-atom reaction. Direct LIF detection of C_2O in these two setups are currently underway.[19] Finally, the observation of OH(A) chemiluminescence in these experiments provide evidence for the (CH + OH) product channel in the CH_2 + O reaction.

ACKNOWLEDGMENT

Funding for this work was provided by the Air Force Office of Scientific Research, and carried out at the Air Force Research Laboratory, Edwards AFB, CA, under Contract No. F04611-93-C-0005.

REFERENCES

1. Renlund, A. M.; Shokoohl, F.; Reisler, H.; Wittig, C., "Reaction of C_2H With O_2: Chemiluminescent Products," *J. Phys. Chem.* **1982**, *86*, 4165.

2. Bauer, W.; Becker, K. H.; Meuser, R., "Laser Induced Fluorescence Studies on C_2O and CH Radicals," *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 340.

3. Becker, K. H.; Bayes, K. D., "CO Chemiluminescence From Flames," *J. Chem. Phys.* **1968**, *48*, 653.

4. Bayes, K. D., "Spectroscopic Study of the Chemiluminescent Reaction O + CCO," *J. Chem. Phys.* **1970**, *52*, 1093.

5. Becker, K. H.; Horie, O.; Schmidt, V. H.; Wiesen, P., "Spectroscopic Identification of C_2O Radicals in the C_3O_2 + O Flame System By Laser-Induced Fluorescence," *Chem. Phys. Lett.* **1982**, *90*, 64.

6. Fontijn, A.; Johnson, S. E., "Mechanism of CO Fourth Positive vuv Chemiluminescence in the Atomic Oxygen Reaction With Acetylene. Production of $C(^3P, ^1D)$," *J. Chem. Phys.* **1973**, *59*, 6193, and Fontijn, A.; Fernandez, A.; Ristanovic, A.; Randall, M. Y.; Jankowiak, J. T., "CO Chemiluminescence and Kinetics of the C_2 + O_2 Reaction," *J. Phys. Chem.* **2001**, *105*, 3182,

7. Burke, M. L.; Dimpfl, W. L.; Sheaffer, P. M.; Zittel, P. F.; Bernstein, L. S., "Formation of Triplet CO in Atomic Flames of Acetylene and Carbon Suboxide," *J. Phys. Chem.* **1996**, *100*, 138.

8. Renlund, A. M.; Shokoohl, F.; Reisler, H.; Wittig, C., "Gas-Phase Reactions of $C_2H(X^2\Sigma^+)$ With O_2, H_2, and CH_4 Studied via Time-Resolved Product Emissions," *Chem. Phys. Lett.* **1981**, *84*, 293.

9. Devriendt, K.; Van Look, H.; Ceursters, B.; Peeters, J., "Kinetics of Formation of Chemiluminescent $CH(A^2\Delta)$ by the Elementary Reactions of $C_2H(X^2\Sigma^+)$ With $O(^3P)$ and $O_2(X^3\Sigma_g^-$): A Pulsed Laser Photolysis Study," *Chem. Phys. Lett.* **1996**, *261*, 450.

10. Boullart, W.; Devriendt, K.; Borms, R.; Peeters, J., "Identification of the Sequence $CH(^2\Pi)$ + $C_2H_2 \rightarrow C_3H_2$ + H (and C_3H + H_2) Followed by C_3H_2 + O $\rightarrow$ C_2H + HCO (or H + CO) as C_2H Source in C_2H_2/O/H Atomic Flames," *J. Phys. Chem.* **1996**, *100*, 998.

11. Vaghjiani, G. L., "Discharge Flow-tube Studies of $O(^3P)$ + N_2H_4 Reaction: The Rate Coefficient values over the Temperature Range 252-423 K and the $OH(X^2\Pi)$ Product Yield at 298 K," *J. Chem. Phys.* **1996**, *104*, 5479.

12. Vaghjiani, G. L., "140-400 nm Absorption Cross Sections of Ketene and Products During Laser Photodissociation," *J. Chem. Phys.* **2001**, to be submitted.

13. Howard, C. J., "Kinetic Measurements Using Flow Tubes," J. Phys. Chem. **1979**, *83*, 3, and references therein.

14. Vaghjiani, G. L., "Laser Photolysis Studies of Hydrazine Vapor: 193 and 222-nm H-atom Primary Quantum Yields at 296 K, and the Kinetics of H + N_2H_4 Reaction Over the Temperature Range 222-657 K," *Int. J. Chem. Kinet.* **1995**, *27*, 777.

15. Carr, R. W.; Gay, I. D.; Glass, G. P.; Niki, H., "Reaction of Ketene With Atomic Hydrogen and Oxygen," *J. Chem. Phys.* **1968**, *49*, 846.

16. Mack, G. P. R.; Thrush, B. A., "Reaction of Oxygen Atoms With Carbonyl Compounds," *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 187.

17. Washida, N.; Hatakeyama, S.; Takagi, H.; Kyogoku, T.; Sato, S., "Reaction of Ketenes With Atomic Oxygen," *J. Chem. Phys.* **1983**, *78*, 4533.

18. Bohland, T.; Temps, F.; Wagner, H. Gg., "Direction Investigation of the Reaction $CH_2(X^3B_1)$ + $O(^3P)$ with the LMR," *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 1222.

19. Vaghjiani, G. L., work in progress, **2001**.

20. Hayden, C. C.; Neumark, D. M.; Shobatake, K.; Sparks, R. K.; Lee, Y. T., "Methylene Singlet-Triplet Energy Splitting by Molecular Beam Photodissociation of Ketene," *J. Chem. Phys.* **1982**, *76*, 3607.

21. Bradley, J. N.; Tse, R. S., "Electron Spin Resonance Study of the Reaction Between Oxygen Atoms and Acetylene," *Trans. Faraday Soc.* **1969**, *6*, 2658.

22. Messing, I.; Sadowski, C. M.; Filseth, S. V., "Absolute Rate Constant for the Reaction of CH With O_2," *Chem. Phys. Lett.* **1979**, *66*, 9.

23. Messing, I.; Filseth, S. V.; Sadowski, C. M.; Carrington, T., "Absolute Rate Constants for the Reactions of CH With O and N Atoms," *J. Chem. Phys.* **1981**, *74*, 3874.